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MECHANISTIC STUDIES OF DETONATION INITIATION:
THE CHEMICAL BEHAVIOR OF
SHOCKED ORGANIC HALIDES

ROBERT D. BUCHWALD
and
JIMMY F. SMITH

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THE CHEMICAL BEHAVIOR OF SHOCKED ORGANIC HALIDES

* * * * *

Robert D. Buchwald

and

Jimmy F. Smith

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THE CHEMICAL BEHAVIOR OF SHOCKED ORGANIC HALIDES

by

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//

Lieutenant, United States Navy

and

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Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

United States Naval Postgraduate School
Monterey, California

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ABSTRACT

A single-pulse shock tube has been designed, constructed and used to study the kinetics of methyl iodide and ethyl iodide pyrolysis in the range 2700-2900 °K. For methyl iodide the chief products are methane, ethylene, acetylene and iodine and for ethyl iodide they are the same plus ethane. The experimental data seem to support a mechanism in methyl iodide pyrolysis that is free-radical in nature and involves one activation step. In the ethyl iodide case there appear to be two separate free-radical activations, one involving cleavage of the carbon-carbon bond and the other that of the carbon-iodine bond.

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INTRODUCTION

It is necessary that the initial molecular events in an explosive detonation be accurately determined in order to construct a more comprehensive model of the detonation process. In the past, kinetic studies have been undertaken through examination of the chemical products of an actual detonation, during which very high temperatures and pressures exist for periods of time long enough to allow the initial species formed to further decompose to the final products of detonation in equilibrium at temperature and pressure different from the actual detonation condition. It has been shown¹ that the passage of a shock wave through a reactant subjects any given molecule to high temperatures and pressures over time intervals in the order of microseconds. It has been postulated that through use of this shock wave energy transfer, the length of time the explosive and initial products are subjected to extreme conditions may be greatly reduced in comparison to an actual detonation. From the information thus obtained a better understanding of the actual explosive reaction mechanism may be gained.

As a first step in the development of the shock wave techniques, an examination of the reaction of two of the simple organic iodides was undertaken.

¹Some leading references on shock tube technology
J. N. Bradley, Shock Waves in Chemistry and Physics, John Wiley & Sons, 1962
A. Ferri, Fundamental Data Obtained From Shock Tube Experiments, Pergamon Press Inc., 1961
E. F. Greene and J. P. Toennies, Chemical Reactions in Shock Waves, Academic Press Inc., 1964

HISTORICAL

The use of shock tubes for the investigation of chemical reactions is a fairly recent innovation. In 1953 Davidson^{2,3} and his coworkers made use of shock wave techniques in the study of the dissociation of N_2O_4 and of I_2 . Optical methods were used to observe the change in opacity with time. Greene⁴ and Penner⁵ and their associates also employed optical techniques for studying gas phase reactions immediately behind a shock front. A non-optical system was developed at the Cornell Aeronautical Laboratory by Glick⁶, Klein and Squire for study of the reaction $N_2 + O_2 = 2NO$. The reactant gases are processed by a single high temperature pulse and rapidly cooled by expansion waves. With a sufficiently high cooling rate the reaction rates can be reduced so rapidly that the reactant mixture is "frozen" and many of the products that exist immediately after shock passage remain for later analysis and resulting study of high temperature kinetics.

²T. Carrington and N. Davidson, J. Phys. Chem. 57, 418-427 (1953)

³D. Britton, N. Davidson, and G. Schott, Discussions Faraday Soc. 17, 58 (1954)

⁴E. F. Greene, J. Am. Chem. Soc. 76, 2127 (1954)

⁵S. Penner, F. Harshbarger, and V. Vali, "An introduction to the use of the shock tube for the determination of physico-chemical parameters" (CalTech Jet Propulsion Center Report AD 95210 AFOSR TN-56- 334, June, 1956)

⁶H. S. Glick, J. J. Klein, and W. Squire, J. Chem. Phys. 27, 850 (1957)

Skinner^{7,8,9} and coworkers have examined the pyrolysis of methane, ethane and ethylene at temperatures ranging from 1000° - 1800° K using a shock tube similar to the one at Cornell. Other workers have made similar studies of the same hydrocarbon systems. In all of these hydrocarbon studies, argon was used as a diluent and total initial pressures in the reaction zone were in the order of five atmospheres. At the lower range of temperatures investigated, the major products from methane pyrolysis were hydrogen, ethane and ethylene while at higher temperatures the major products were hydrogen, ethylene and acetylene. In ethane pyrolysis, higher temperatures favored acetylene and methane formation rather than the ethylene produced at lower temperatures. Skinner suggested that the methane is derived directly from ethane and not from ethylene or acetylene intermediates.

In their investigation of the pyrolysis of ethylene, Skinner⁹ and Sokoloski found hydrogen and acetylene as the major products and suggested that formation of the latter is a molecular and not a radical reaction.

The pyrolysis of the organic iodides has been investigated only at moderate temperatures in the order of 600-700°K and at comparatively long reaction times of an hour or more. Benson^{10, 11} and associates have done

⁷ G. B. Skinner and R. A. Ruehrwein, J. Phys. Chem. 63, 1736 (1959)

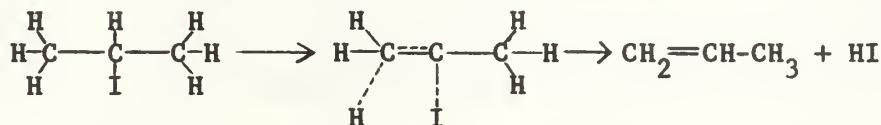
⁸ G. B. Skinner and W. E. Ball, J. Phys. Chem. 64, 1025 (1960)

⁹ G. B. Skinner and E. M. Sokoloski, J. Phys. Chem. 64, 1028 (1960)

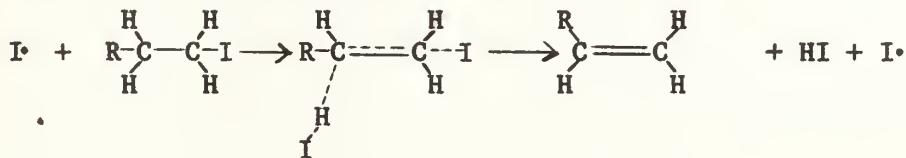
¹⁰ S. W. Benson and A. N. Bose, J. Chem. Phys. 37, 2935 (1962)

¹¹ S. W. Benson, J. Chem. Phys. 38, 1945 (1962)

most of the recent work and have suggested kinetic mechanisms for the pyrolysis of methyl, ethyl, n-propyl and 2-propyl iodides. It would appear from their work that in cases where the iodine atom is attached to a secondary or tertiary carbon, that the fastest process is a genuine four center, molecular reaction, i.e., spontaneous HI elimination leading to formation of the olefin.



For the primary iodides, however, a fast competing step appears to be an iodine atom catalyzed elimination with an activation energy which is just equal to the endothermicity of the process. It is therefore possible that in abstraction of the alpha hydrogen from the parent iodide, a concerted process takes place in which the double bond is formed and the iodine atom eliminated in one step.



Additional work done by Benson^{12,13} and associates has led to revision of the heat of formation of the ethyl and 2-propyl radicals in accordance with newly established values for the carbon-iodine bond dissociation energy in ethyl iodide and 2-propyl iodide.

¹²D. B. Hartley and S. W. Benson, J. Chem. Phys. 39, 132 (1963)

¹³P. Nangia and S. W. Benson, J. Am. Chem. Soc. 86, 2773, (1964)

EXPERIMENTAL

EQUIPMENT

The experimental assembly consists of four components; the primary reaction vessel (the shock tube), the collection apparatus, the volume manifold, and the chromatograph and I. R. spectrometer for product analysis.

The primary reaction vessel is a 7.65 centimeter diameter stainless steel shock tube with driver and reaction sections 75.1 and 227.8 centimeters in length, respectively. The total volume of the reaction section is 10.540 liters. Two ENDEVCO Model 2501 pressure transducers spaced 63.5 centimeters apart near the downstream end of the reaction section are used for measuring the incident shock speed. Two identical circuits amplify the transducer signals which are used to trigger and stop a Potter Model 456 timer, accurate to 0.10 microsecond. A stainless steel diaphragm of .004 inch thickness separates the driver and reaction sections of the shock tube. External piping and fittings which connect directly to the shock tube are stainless steel. These lines lead to the vacuum pump, helium supply, and the collecting system. (See Fig. 1)

The sample under study is evaporated from the collecting system into the reaction section until the pressure is about 10 millimeters of Hg. The driver section is pressurized to about 200 psig by admitting helium gas from an exterior tank. The shock wave is then initiated by rupturing the diaphragm with a push rod which extends through the end plate of the shock tube. The push rod enters the shock tube through a packing gland and is driven forward by a jack-screw mechanism turned by a crank. A slight thrust from the rod is sufficient to cause failure of the diaphragm since it has already been stressed almost to the bursting point by the pressure

in the driver section. Shock speed deviations of less than 1% were obtained by this method of rupturing the diaphragm. Reaction conditions were thus held essentially constant for successive experimental runs.

The shock wave forms and moves down the tube, actuating first the starter and then the stopping transducer for the timer. The helium mass following the shock wave then catches and cancels it near the end plate, either before or after reflection (cf. discussion). The static pressure in the shock tube after reaction is about 40 psig and is throttled to the collecting system through a stainless steel needle valve.

The collection apparatus consists of five glass-U-tube traps cooled by liquid air in Dewar flasks, a manometer for measuring the pressure in the system, a sample tube containing the experimental compound, and a vacuum pump for mass transfer of the driver gas during work up. As shown in Fig. 2, the first three traps are stationary and can be isolated by closing stop-cocks at each end of the trio. The fourth in line, or transfer trap, can also be isolated and is used to collect all the product gases to be removed to the volume manifold. The fifth trap is used as protection for the collection system and does not collect product gases.

The gases in the shock tube, at about 40 psig, are throttled into the collection system at such a rate as to minimize removal time as well as to minimize carryover loss of condensed products. The liquid-air-cooled traps collect the reaction products while allowing the helium carrier gas and any hydrogen formed in the reaction to be discharged to the atmosphere.

After all reaction gases have been removed from the shock tube, the first four U-tubes are isolated from the remainder of the system. Removal of the Dewar flasks of liquid air from the first three tubes allows the product gases to distill into the transfer trap. The three stationary tubes

and the transfer trap are then separately isolated. The transfer trap containing the condensed product gases is removed to the volume manifold. Some of the iodine obtained in the reaction does not distill into the transfer trap and remains in the stationary trio. This iodine is dissolved in carbon tetrachloride and titrated with standard sodium thiosulfate.

The volume manifold is a standard high vacuum glass system in which a proportional gas sample of measured volume, temperature and pressure may be obtained. It contains a Toepler pump for pumping gas samples, a vacuum pump for rough pumping and another for fine pumping, three separate manifolds of 290 cubic centimeters volume, a manometer for measuring pressure differentials, and a "christmas tree" with gas burette for measuring gas volume. The transfer trap is connected to the volume manifold and the reaction products evaporated into the system. The gas sample referred to above is collected for chromatographic analysis at a pressure greater than atmospheric. The vessel used has a rubber septum connection allowing a sample to be taken by a hypodermic syringe for insertion into the product analysis chromatograph. The sample is taken at a pressure greater than atmospheric to exclude air contamination during syringe transfer of the portion to be analyzed.

ANALYSIS

Primary gas analysis was made using a Beckman GC1 gas chromatograph and comparing holdup times on gas-liquid partition columns against calibrated holdup times for known gases. A Beckman 17297 Gas-Liquid partition chromatographic column consisting of a 12-foot length of $\frac{1}{4}$ -inch copper tubing, filled with 30 grams of crushed firebrick coated with 12 grams of reagent grade benzyl ether, was used for separation and analysis of organic gases of molecular weight greater than propane. This column has a specificity for unsaturated compounds, which follow corresponding saturated compounds in order of elution. Another column consisting of a 6-foot length of $\frac{1}{4}$ -inch copper tubing, filled with 90% by mass of activated Silica Gel and 10% Kromat firebrick, was used for separation of the lower molecular weight organic gases up to and including propane. A separate syringe sample was used for each column. Column temperatures for all runs was constant at 105°F. Holdup times for calibration gases are given in Table 1. The chromatograph output was recorded on a Leeds and Northrup Speedomax type G recorder.

The chromatograph was calibrated by using known gases and measuring holdup times for each of the two columns used. The silica gel column was used to separate and analyze methane, ethane, ethylene, propane, propylene and acetylene. The benzyl ether column was used primarily to separate these gases from the four- and five-carbon compounds. It also separated butane, the butenes, methyl and ethyl acetylene, and neopentane. Both columns used helium as the carrier gas. Sufficient sensitivity was obtained to detect trace amounts in the order of a tenth of a percent.

An Infracord Model 337 was used to obtain relative extinction coefficients of gaseous samples and analyze for Methyl and Ethyl Iodide as well

as to check on the qualitative chromatographic results. Spectra of typical runs for both compounds studied may be found in Figs. 3-4.

TYPICAL RUN.

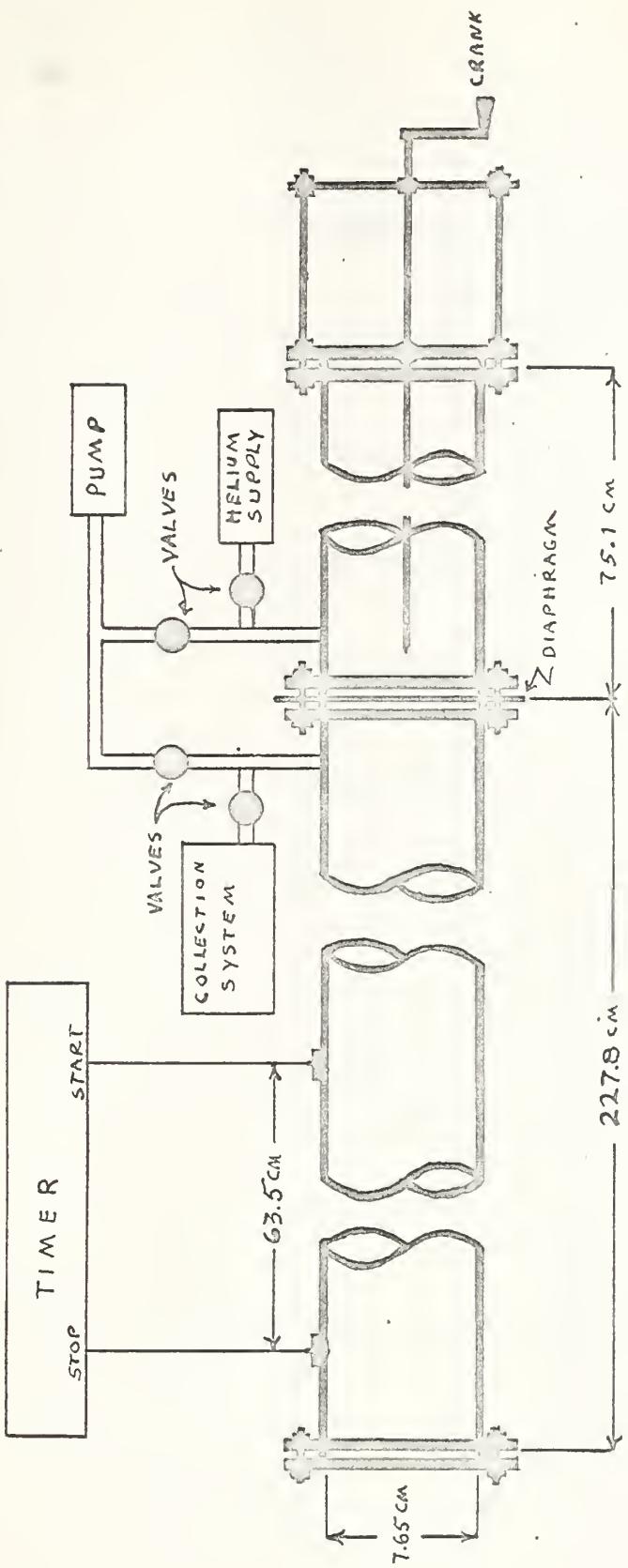
In a typical run, all sections of the shock tube were first evacuated. Then the sample was evaporated into the reaction chamber in order to give the desired pressure (approximately 10 mm Hg). After any system containing glass was thoroughly sealed off from the steel shock tube, the driver gas (helium) was introduced into the driver section of the tube until the pressure reached the desired driver value (about 200 psig). The tube was then closed off from all external piping and the diaphragm ruptured. The shock wave formed, moved down the tube, (thereby activating first the start-trigger transducer and then the stopping transducer), hit the end of the tube and was cancelled by the helium mass following, either before or after reflection.

The valves leading to the collection system were then opened to give a slow flow through the four liquid-air-cooled collection tubes. The helium driver gas passed on through to the atmosphere while the product gases were collected as liquids or solids. After the shock tube was down to its original pressure and all product gases had been collected, the collection system was isolated from the tube and the pump, and allowed to distill into the transfer trap by carefully removing the liquid-air-filled Dewar flasks from the stationary trio. After the latter had been allowed to come to room temperature and the sample gases had been collected in the transfer trap, the three stationary tubes were again isolated and carbon tetrachloride introduced to dissolve the residual iodine. The transfer trap was taken to the volume measuring manifold where a known proportion (at a known temperature,

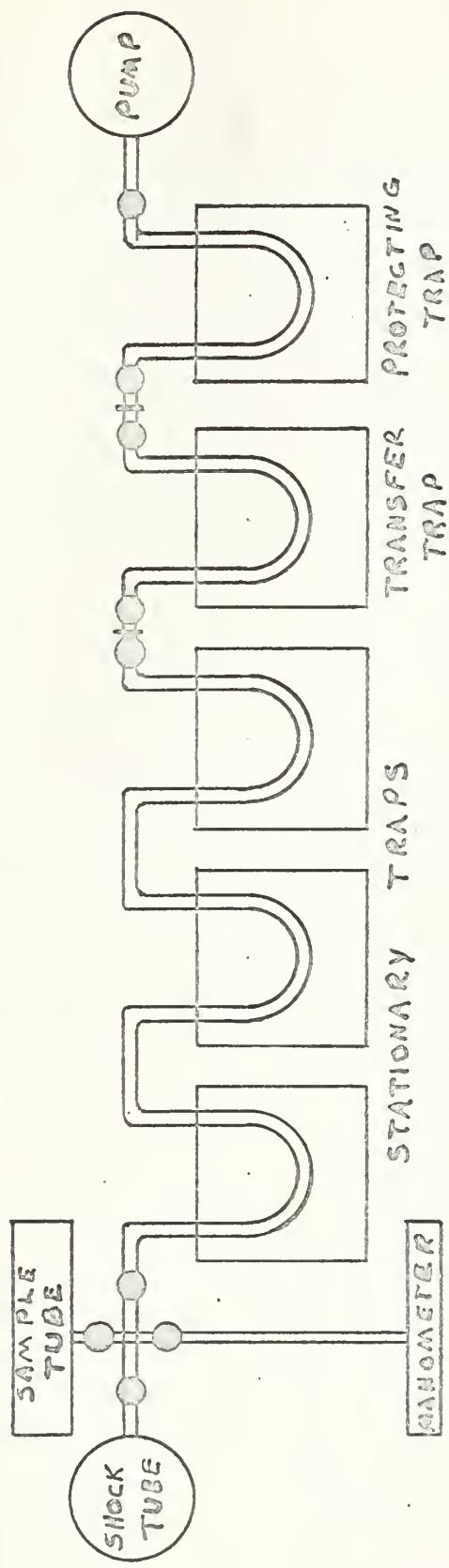
volume and pressure) was taken into the sample tube for transfer to the vapor phase chromatograph for analysis. Another sample was taken into the gas sample cells for analysis on the Infracord. The elapsed time from the initial passage of the shock wave until all reaction products were collected at liquid air temperatures was about 3 hours.

RESULTS

A total of seventeen preliminary firing runs were made with the shock tube in order to evaluate the optimum firing pressure, diaphragm thickness and accuracy of the timer. Results of the actual experimental runs are presented in Tables 2-4. Products noted in the methyl iodide trials were methane, ethylene, acetylene, and iodine while in ethyl iodide runs ethane was also observed. No provision was made to analyze for hydrogen. It should be noted that I.R. spectra showed no evidence of HI formation in either case.



SHOCK TUBE
FIG 1



COLLECTION SYSTEM

FIG. 2

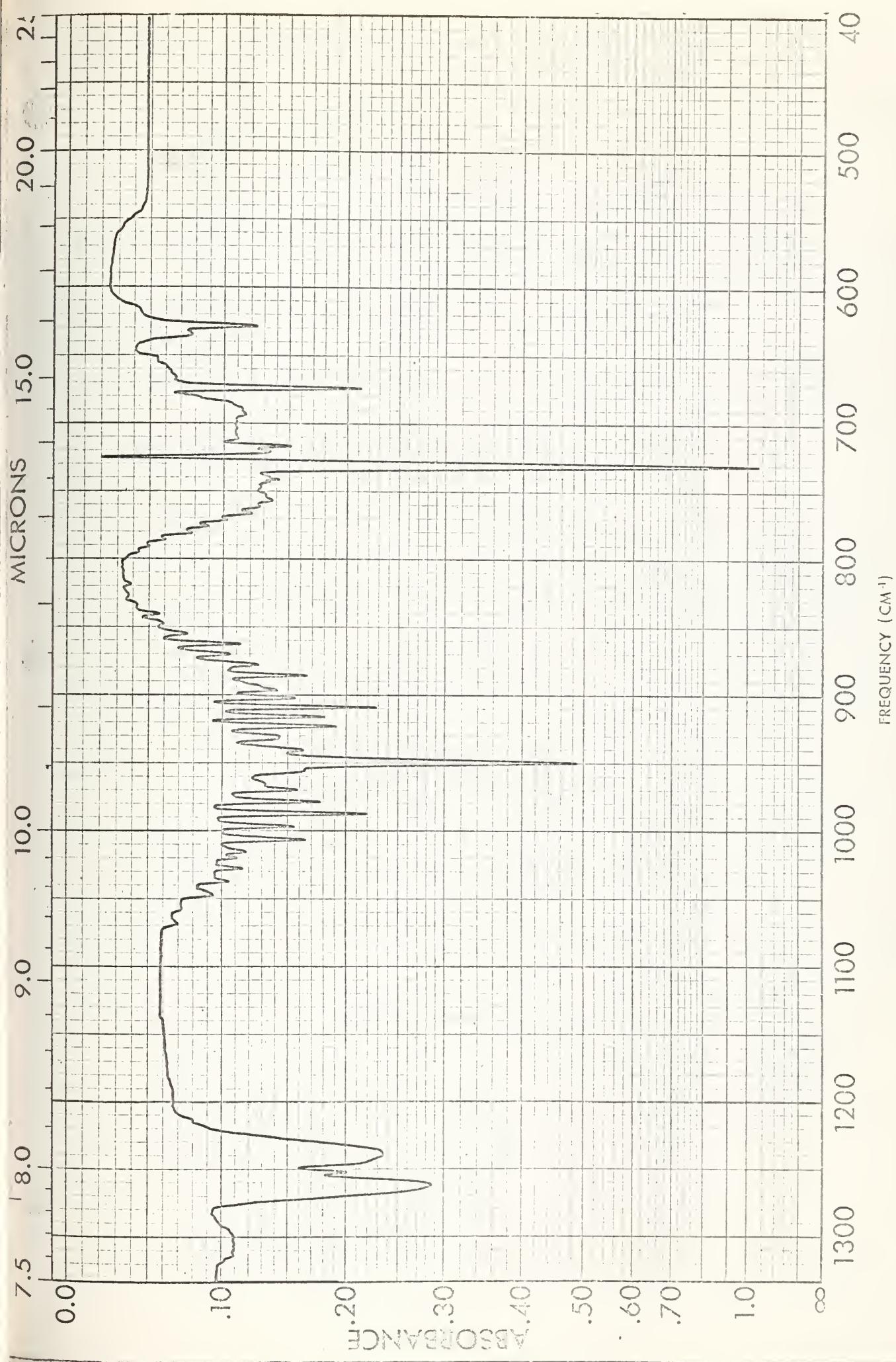


FIG. 3(3) IR SPECTRUM OF TYPICAL METHYL LACTATE ESTER PHASE

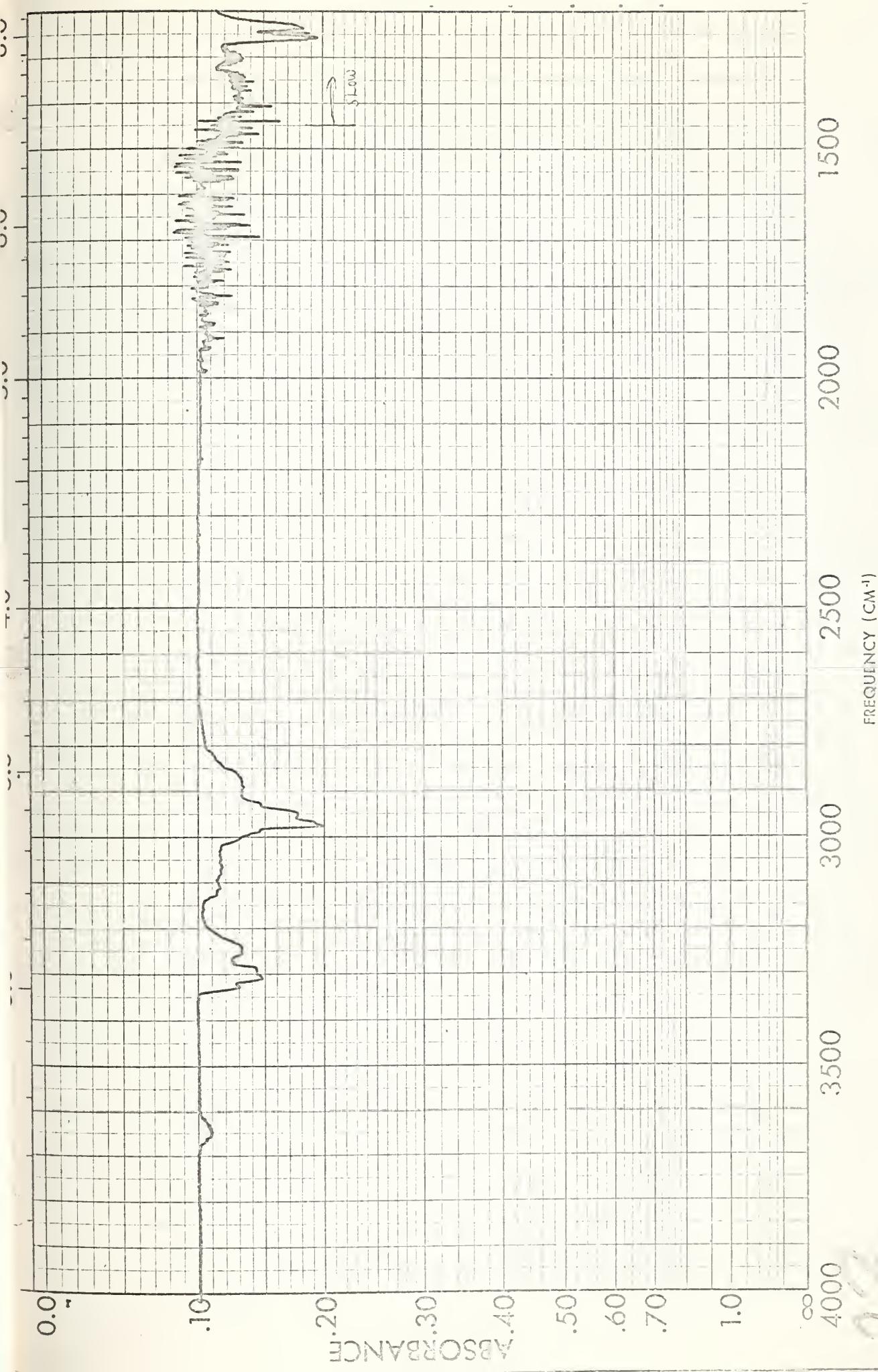


FIG 2(b) IR SPECTRUM OF TYPICAL METHYL IODIDE RUN (GAS PHASE)

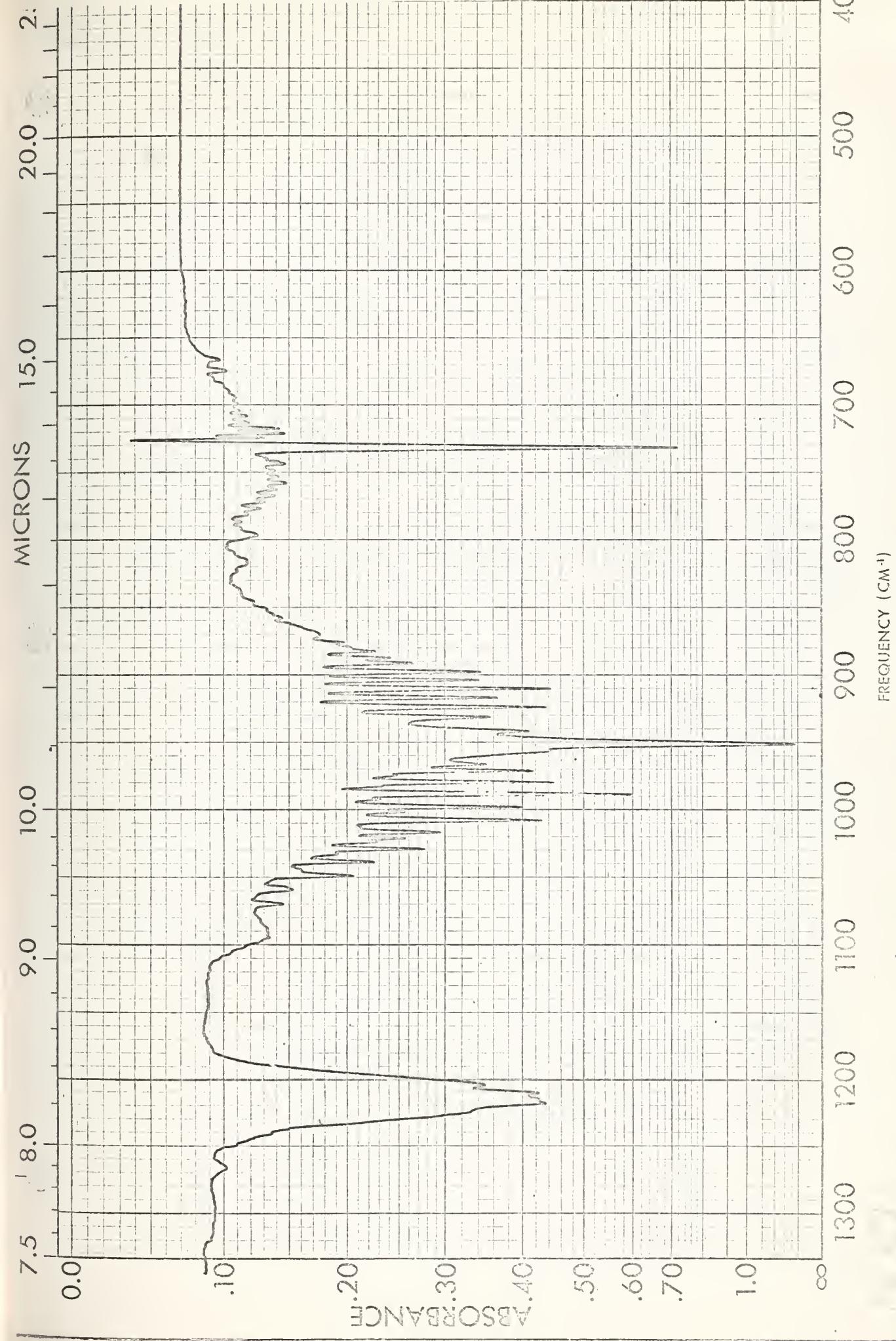


FIG. 4(4) IR SPECTRUM OF TYPICAL ETHYL IODIDE RUN (GAS PHASE)

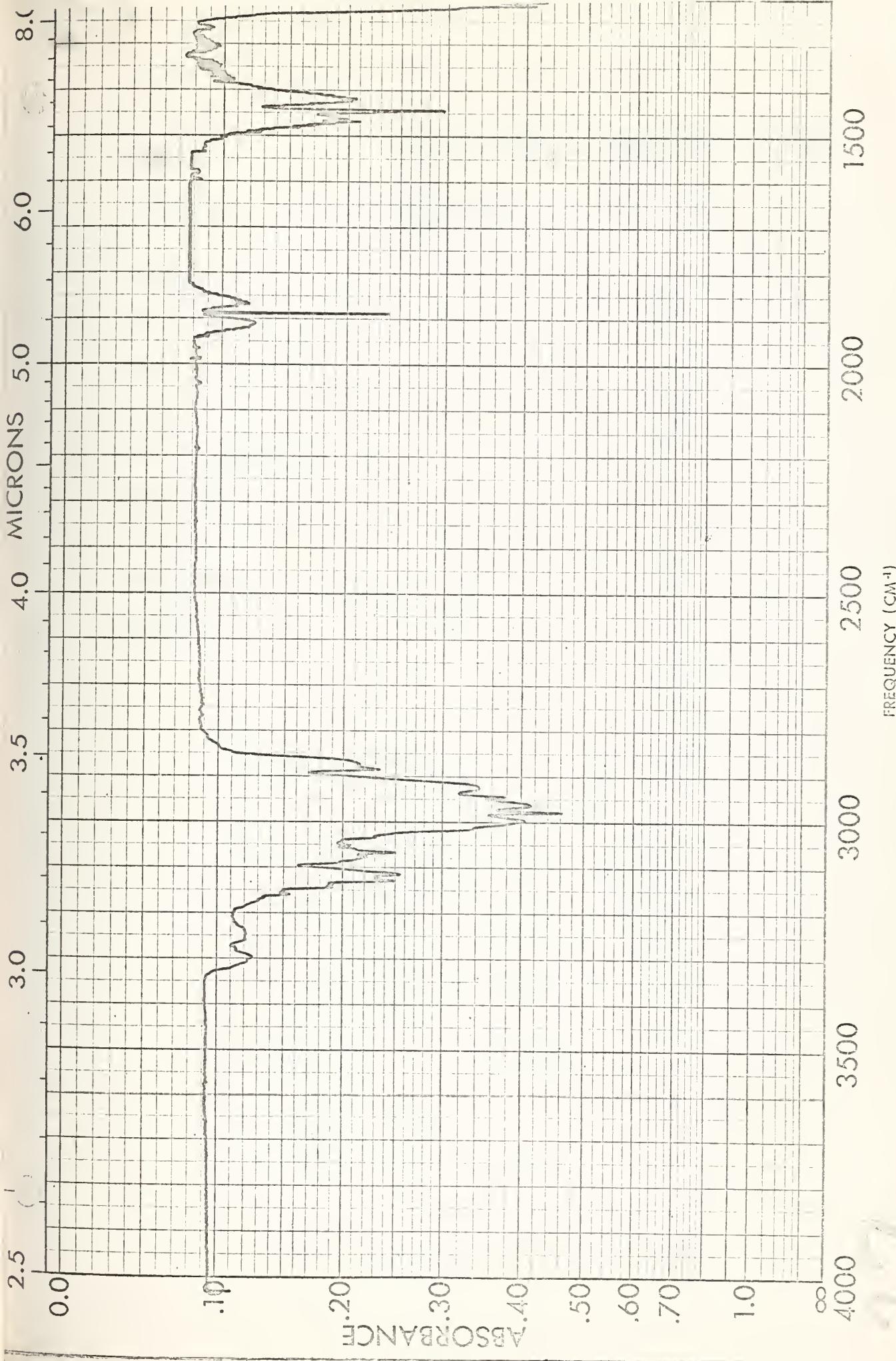


FIG. 4(b) IR SPECTRUM OF TYPICAL ETCH, IODIDE RUN (GAS PHASE)

TABLE 1**RETENTION TIMES IN CHROMATOGRAPH COLUMNS**

Sample gas	Benzyl ether column, sec.	Silica gel column, sec.
Methane	148	35
Acetylene	200	1250
Ethylene	171	445
Ethane	171	238
Methyl Acetylene	---	---
Propylene	205	---
Propane	182	---
Isobutane	260	---
Butane	344	---

TABULATION OF DATA

TABLE 2 METHYL IODIDE RUNS

<u>RUN</u>	<u>MOLES OF REACTANT</u>	<u>DRIVER PRESS.</u>	<u>REACTANT GAS PRESSURE (mm Hg)</u>	<u>TIMER READ. (sec. X 10³)</u>	<u>SHOCK SPEED (ft/sec.)</u>	<u>MOLES 1/2 RECOVD.</u>	<u>MOLES PHASE PRODUCTS</u>	<u>TOTAL MOLES PRODS.</u>
1	----- .0106	192	18.6	.58375	3570	.00097	-----	-----
2	.0114 .0103	187	18.1	.58000	3590	.00093	-----	-----
3	.0123 .0113	187	19.7	.591125	3520	.00095	-----	-----
4	.00539 .00515	188	9.0	-----	-----	.00027	.00440	.00467
5	.00700 .00634	170	11.1	.99813	2090	.00086	.00305	.00391
6	.00576 .00565	188	9.9	.50875	4080	.00064	.00220	.00284

TABLE 2. (CONT'D)

<u>RUN</u>	<u>MOLES PROD. PER MOLE OF REACTANT</u>	<u>MOLES GAS PHASE PROD. PER MOLE REACTANT</u>	<u>MOLES METHYL IODIDE RECOVERED</u>	<u>PERCENT RECOVERY AS I₂</u>	<u>OVERALL PERCENT RECOVERY OF IODINE</u>	<u>PERCENT METHYL IODIDE REACTION</u>
1	-----	-----	-----	18.3	-----	-----
2	-----	-----	-----	17.2	-----	-----
3	-----	-----	-----	16.1	-----	-----
4	.89	.84	.000826	10.3	26.0	84.3
5	.62	.46	.000389	25.7	31.5	94.2
6	.50	.39	.000362	22.5	28.8	93.7

TABLE 3. ETHYL IODIDE RUNS

RUN	MOLES OF REACTANT	DRIVER PRESS. (PSIG)	REACTANT GAS PRESSURE (mm Hg)	TIMER READ. (sec) $\times 10^3$	SHOCK SPEED (ft/sec)	MOLES I ² RECOVERED	MOLES GAS PHASE PRODUCTS	TOTAL MOLES PRODUCT
1	.01173 .01135	193	19.7	.61188	3400	.00082	-----	-----
2	.00562 .00564	180	9.9	.60000	3475	.00047	.00847	.00894
3	.00453 .00513	187	9.0	-----	-----	.00066	.00735	.00801
4	.00633 .00571	188	10.0	-----	-----	.00064	.00550	.00614
5	.00540 .00513	160	9.0	.55938	3730	.0056	.01015	.01071

TABLE 3. (CONT.)

<u>RUN</u>	<u>MOLES PROD. PER MOLE OF REACTANT</u>	<u>MOLES GAS PHASE PROD. PER MOLE REACTANT</u>	<u>MOLES ETHYL IODIDE RECOVERED</u>	<u>PERCENT RECOVERY AS I₂</u>	<u>OVERALL PERCENT RECOVERY OF IODINE</u>	<u>PERCENT ETHYL IODIDE REACTION</u>
1	-----	-----	-----	14.2	-----	-----
2	1.58	1.50	.000182	16.5	19.9	96.8
3	1.66	1.52	.000116	27.3	29.8	97.5
4	1.02	.92	.000122	21.3	23.3	97.9
5	2.03	1.93	.000592	21.3	32.5	88.8

TABLE 4SUMMARY OF GASEOUS PRODUCT ANALYSISMETHYL IODIDE RUNS

<u>RUN NO.</u>	<u>METHANE (%)</u>	<u>ETHYLENE (%)</u>	<u>ACETYLENE (%)</u>
4	57.9	17.8	24.5
5	60.5	21.6	17.9
6	40.6	25.6	33.9
Avg. 4 & 5	59.2	19.7	21.2
Avg. 4,5 & 6	53.0	21.7	25.4
Approx. Ratio	3	1	1

ETHYL IODIDE RUNS

<u>RUN NO.</u>	<u>METHANE (%)</u>	<u>ETHANE (%)</u>	<u>ETHYLENE (%)</u>	<u>ACETYLENE (%)</u>
2	30.3	13.5	48.0	8.3
3	50.0	7.4	42.6	trace
4	31.8	12.5	44.4	8.6
5	32.5	10.9	49.6	7.0
Avg. 2,4,& 5	31.5	12.3	47.3	8.0
Approx. Ratio	4	1.5	6	1

DISCUSSION

The average shock wave velocity was approximately 3600 feet per second for all runs indicating mach numbers (see Table 6) in the methyl iodide and ethyl iodide of 7.4 and 8.0 respectively. Utilizing Ferri's graphical relationships¹⁴, translational temperatures in the incident shock wave were determined to be about 2700°K for the methyl iodide runs and 2940°K for ethyl iodide runs. Bradley¹⁵, in his review of the work of L. H. Thomas, has shown that the expected shock wave thickness should be about 1.8 mean free paths. At the velocities measured this leads to stay times in the order of 2-6 nanoseconds. For the purpose of this work, stay time is defined as the length of time to which the reactant molecules are subjected to the extreme translational temperatures indicated, i.e., the length of time it takes for the shock front to pass. It is believed that the reflected shock wave experienced in many shock tubes is not a significant factor here due to the fact that the average kinetic theory velocity of the helium atoms at ambient temperature is such that the shock wave will be overtaken near the downstream end of the tube with resultant turbulence and eventual collapse of the shock front. In several of the runs the downstream transducer was not actuated and, as a result, the timer was not stopped. A possible explanation for this behavior could be that the shock front may have already collapsed leaving no strong pressure pulse to actuate the final transducer. In view of the foregoing argument and an extension of the temperature dependence of Benson's work (cf. below),

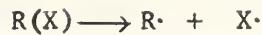
¹⁴ cf. Ferri, loc. cit., page 100

¹⁵ cf. Bradley, loc. cit., page 86

it is felt that the only energy transfer of importance is that indicated for the incident shock wave.

Various bond dissociation energies of importance to a discussion of possible kinetic meachanisms are listed in Table 5. Heat of formation data was taken from NBS Circular No. 500.

TABLE 5



BOND	BOND DISSOCIATION ENERGY (D) @ 0 °K (kcal)
CH ₃ (H)	101-102
C(H)	80
CH ₂ (H)	87
CH(H)	123
CH ₃ CH ₂ (H)	97
•CH ₂ CH ₂ (H)	37
CH ₃ (CH ₃)	83- 85
CH ₂ CH(H)	104
•CHCH(H)	39
CH ₂ (CH ₂)	122
CHC(H)	114
•CC(H)	136
CH(CH)	228
H(H)	104
C ₂	141
I(I)	36
CH ₃ (I) ^a	55
CH ₃ CH ₂ (I)	53
H(I)	71

^aAll but the last three values in the above table were taken from the review of bond dissociation energies by B. E. Knox and H. B. Palmer, Chem. Reviews 59, 247 (1960). The figures given for the carbon-iodine bond in methyl and ethyl iodide are from Benson's work. The value for HI is from NBS Circular No. 500.

TABLE 6

MACH NUMBERS, MEAN FREE PATH AND STAY TIME

<u>REACTANT</u>	<u>SPECIFIC HEAT RATIO</u>	<u>SPEED OF SOUND (ft/sec)</u>
CH ₃ I	1.28	487
CH ₃ CH ₂ I	1.21	452

MACH NUMBERS

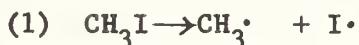
<u>RUN NO.</u>	<u>METHYL IODIDE</u>	<u>ETHYL IODIDE</u>
1	7.34	7.52
2	7.38	7.80
3	7.23	no time
4	no time	no time
5	4.31	8.25
6	8.40	
7	8.00	

<u>REACTANT</u>	<u>MEAN FREE PATH^a (cm.)</u>	<u>STAY TIME (sec.)</u>
CH ₃ I	3.86 X 10 ⁻⁴	6.3 X 10 ⁻⁹
CH ₃ CH ₂ I	1.43 X 10 ⁻⁴	2.4 X 10 ⁻⁹

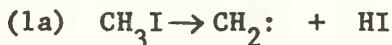
^aCalculated at 23°C. and 10 mm pressure from kinetic theory

Very little attention has been given in the literature to the pyrolysis of the simplest organic iodide. Benson¹¹ has postulated a possible mechanism based on theory and some of his own work on the more complex iodides (see Fig. 5). It must be remembered, however, that all of his experiments involved reaction times of approximately an hour or more. Since, in the shock tube, the individual molecules are at the extreme temperatures and pressures for such a comparatively short time, it will be assumed here that only one activation step occurs in the individual molecular reaction sequence.

In the case of the methyl iodide the initial activation can proceed in either or both of two ways. The molecule can split into a methyl radical and an iodine atom (cf. equation 1). The energy required is approximately



55 kcal per mole. The second route leads to the formation of methylene diradical and hydrogen iodide (cf. equation 1a). If the loss of hydrogen iodide is considered as a sequential rather than a concerted step the energy



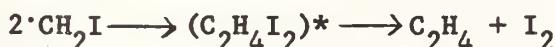
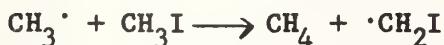
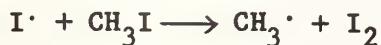
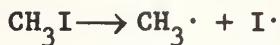
required is about 71 kcal per mole. Although energy requirements would predict reaction (1a) to be less probable than (1) it must be considered in light of Peters¹⁵ molecular orbital treatment of methane photolysis. He shows that the concerted loss of H₂ to form the methylene diradical occurs with a probability of about 0.33 relative to loss of H as one. Energy considerations related to bonds broken would predict an even higher probability for the concerted loss of HI from methyl iodide. In considering

¹⁵D. Peters, J. Chem. Phys. 41, 1046 (1964).

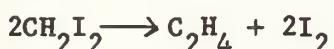
FIG. 5

MECHANISMS FOR THE PYROLYSIS OF METHYL AND ETHYL IODIDE
AS SUGGESTED BY S. W. BENSON

METHYL IODIDE

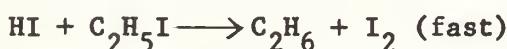
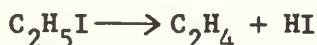


Overall reaction predicted in two stages as follows:

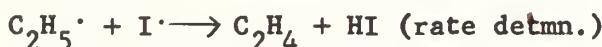
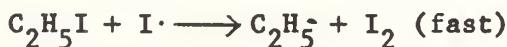


ETHYL IODIDE

Four center molecular dehydrohalogenation



Free radical mechanism

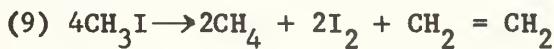


the activated intermediate, however, the H-H bond is being formed as the two C-H bonds are being stretched or broken. Energy gained in the H-H formation lowers the activation energy. In the methyl iodide case the assisting energy gained in the HI formation is not as great. There is thus a lower probability of climbing over the energy barrier leading to methylene. In addition, it is a well known fact that methylene radicals insert as well as add which would lead in our experiments to ethyl iodide, ethane, propane and cyclopropane as products. None of these was observed.

With the assumption of only one activation step all further reaction sequences must be either energetically downhill or of about equal energy (eg. radical interchange). The most important steps should be:

- (1) $\text{CH}_3\text{I} \longrightarrow \text{CH}_3\cdot + \text{I}\cdot$ 55 kcal
- (2) $\text{CH}_3\cdot + \text{CH}_3\text{I} \longrightarrow \text{CH}_3\text{I} + \text{CH}_3\cdot$ time delay only
- (3) $\text{CH}_3\cdot + \text{CH}_3\text{I} \longrightarrow \text{CH}_4 + \text{CH}_2\text{I}\cdot$ -10 kcal
- (4) $2\text{CH}_2\text{I}\cdot \longrightarrow \text{I}_2 + (\text{CH}_2 = \text{CH}_2)^*$
- (5) $(\text{CH}_2 = \text{CH}_2)^* + \text{M} \longrightarrow \text{CH}_2 = \text{CH}_2 + \text{M}^*$ -77.9 kcal (4) and (5)
- (6) $(\text{CH}_2 = \text{CH}_2)^* \longrightarrow \text{CH} = \text{CH} + \text{H}_2$ -38.1 kcal (4) and (6).
- (7) $\text{I}\cdot + \text{CH}_3\text{I} \longrightarrow \text{CH}_3\cdot + \text{I}_2$ approx. 0
- (8) $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$ -142 kcal

where * indicates vibrationally excited molecules which may also be electronically excited. This sequence of reactions explains our observation of methane, ethylene, acetylene and iodine and the absence of all others. No provision was made for analysis of H_2 . Since all acetylene produced is assumed to come from the ethylene, the overall ratio of methane/ethylene-acetylene is theoretically 2/1.



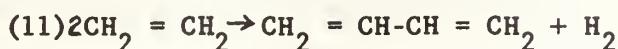
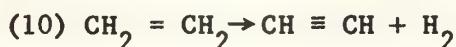
The deviation from the theoretical value and the observed ratio of 1.5/1 is most likely due to the fact that some methane was lost during the three hour pumping cycle (10 mm Hg vapor pressure at liquid air temperatures). Considering this loss it would appear that the experimental data correlates reasonably with theoretically predicted values. Referring to Table 7 we notice the average number of moles of ethylene-acetylene per mole of methyl iodide was 0.28 which also compares favorably with expected values.

A solid blackish-brown compound was deposited on the walls of the shock tube in a very thin coating during the methyl iodide runs. Routine analysis showed the compound to contain iodine. In his experiments Benson noted similar material which he called a "polymer" of carbon and iodine. The low percentage recovery of iodine was due partly to the formation of this compound and partly due to the fact that iodine vapor, collected in the transfer trap, reacted with the mercury in the Toepler pump during product volume measurement.

The mechanism suggested by Benson (see Fig. 5) differs from that proposed above; first, in that it does not postulate acetylene and, second, it shows a step involving the production of methylene iodide. The work on which Benson's predictions were based was done at temperatures of 600-700 °K. He calculates a half life for methylene iodide of about 3 hours¹¹ at a temperature of 673°K. At the much higher temperatures (2700°K) of the shock tube reaction this half life would become negligibly small and no methylene iodide should be obtained. None was observed.

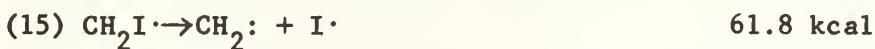
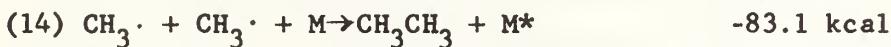
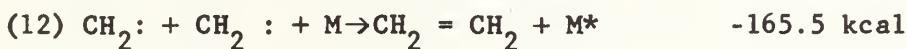
At the temperatures at which Benson conducted his experiments no acetylene was observed. Skinner⁹, in his shock tube work, obtained

acetylene by intramolecular loss of H₂ to form acetylene from ethylene and 1,3-butadiene from dimerization of ethylene.



His temperature range in all experiments was about 1000-1800°K. Absence of butadiene from our products suggests that greater vibrational activation obtained from our higher shock tube temperatures forces the ethylene to react intramolecularly to form acetylene. The formation of butadiene is likely precluded by the greater probability of a non-specific collision to remove energy as compared to the bimolecular collision of two ethylene molecules and subsequent dimerization.

Other important steps which must be considered but were discarded as contributors to the mechanism are:



It is well known that reaction (12) requires a rare set of circumstances and does not readily proceed even in the presence of diluent inert gas. It would provide a route to one of our products but the unlikely production of methylene radicals has been discussed above. It may be a contributor of minor importance.

Reaction (7) is preferred over (13) because of the higher probability of extraction of the iodine substituent due to its polarizability as compared with hydrogen.

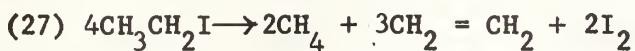
Reaction (14) also requires a three body collision to proceed and, in addition, is less probable than the collision of a methyl radical with a molecule of unreacted methyl iodide. It is clear that the activated complex $(\text{CH}_3\text{CH}_3)^*$ requires the third body for reaction. Hence, it is not surprising that no ethane is found. On the other hand, the collision of two iodomethylene radicals, leading to an activated complex $(\text{CH}_2\text{ICH}_2\text{I})^*$ can proceed by a low energy process to a vibrationally activated ethylene molecule and on to ground state ethylene and acetylene by reactions (5) and (6). Reaction (15) was discarded as improbable due to the energy of activation required.

Proceeding to the somewhat more complex ethyl iodide molecule, we encounter certain significant differences. Benson¹⁰ considered a molecular mechanism (see Fig. 5) as his primary reaction sequence with the radical mechanism of secondary importance. He noted that the radical mechanism gained in importance as the temperature was increased.

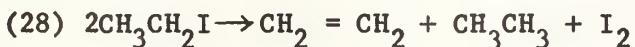
It would appear that the most important steps are:

- | | |
|--|-------------------|
| (16) $\text{CH}_3\text{CH}_2\text{I} \rightarrow \text{CH}_3\cdot + \text{CH}_2\text{I}\cdot$ (activation step) | 86.9 kcal |
| (17) $2\text{CH}_2\text{I}\cdot \rightarrow (\text{CH}_2 = \text{CH}_2)^* + \text{I}_2$ | undetermined |
| (18) $(\text{CH}_2 = \text{CH}_2)^* \rightarrow \text{CH} = \text{CH} + \text{H}_2$ (17 & 18) | -38.1 kcal |
| (19) $\text{CH}_3\cdot + \text{CH}_3\text{CH}_2\text{I} \rightarrow \text{CH}_4 + (\cdot\text{CH}_2\text{CH}_2\text{I})$ | -5 kcal |
| (20) $(\cdot\text{CH}_2\text{CH}_2\text{I}) \rightarrow \text{CH}_2 = \text{CH}_2 + \text{I}\cdot$ | -6 kcal |
| (21) $\text{CH}_3\text{CH}_2\text{I} \rightarrow \text{CH}_3\text{CH}_2\cdot + \text{I}\cdot$ (activation step) | 50.7 kcal |
| (22) $\text{CH}_3\text{CH}_2\cdot + \text{I}\cdot \rightarrow \text{CH}_2 = \text{CH}_2 + \text{HI}$ | -93 kcal |
| (23) $\text{HI} + \text{CH}_3\text{CH}_2\text{I} \rightarrow \text{CH}_3\text{CH}_3 + \text{I}_2$ | -9 kcal |
| (24) $\text{CH}_3\text{CH}_2\cdot + \text{CH}_3\text{CH}_2\text{I} \rightarrow \text{CH}_3\text{CH}_2\text{I} + \text{CH}_3\text{CH}_2\cdot$ | (time delay only) |
| (25) $(\text{CH}_2 = \text{CH}_2)^* + \text{M} \rightarrow \text{CH}_2 = \text{CH}_2 + \text{M}^*$ | undetermined |
| (26) $2\text{I}\cdot \rightarrow \text{I}_2$ | -36 kcal |

In considering the sequence of events resulting from the two possible activation steps, (16) and (21), we may write two independent overall reactions. Combining (16), (17), (19), (20), (25) and (26) we obtain reaction (27).

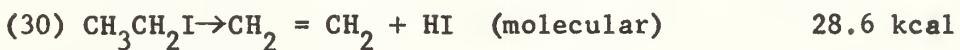
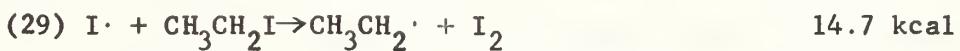


Combining (21), (22) and (23) we arrive at reaction (28).



For comparison purposes, step (18) was not considered in the overall reactions, (27) and (28), due to the assumption that all the acetylene arises from previously produced ethylene. Referring to Table 7 we notice that the average number of moles of ethane and ethylene-acetylene produced per mole of ethyl iodide was 0.14 and 0.68 respectively. Numerical analysis of the data indicates that the activation steps involving the breakage of the carbon-carbon bond accounts for about seven-tenths of the overall reaction.

The following reactions, (29) through (32) were considered to be of minor importance:



Reaction (23) is preferred over (32) due to the greater probability of a collision of HI with an unreacted ethyl iodide molecule rather than with another molecule of HI. Reactions (16) and (19) provide the necessary route to methane which was an observed product. Benson did not detect methane in his ethyl iodide work and noticed no splitting of the carbon-carbon bond. In addition, he predicted simple iodine atom exchange between

methyl and ethyl radical instead of step (19). The carbon-carbon bond is the second weakest bond in the system, however. This fact, coupled with the extreme reaction conditions in the shock tube, would certainly predict methane formation, and, of course, the latter was observed as a major product. Reactions (17) and (18) have been previously discussed (as reactions 5 and 6) as have our reasons for excluding methylene diradical as an intermediate. It should be noted here that the formation of the "polymer" of carbon and iodine was considerably reduced in comparison to the methyl iodide runs.

It is interesting to note that an extension of the temperature dependence of the ethyl iodide pyrolysis using Benson's Arhennius constant and energy of activation predicts temperatures of 2050°K for the time of reaction and percent conversion of starting material noted in our experiments. This is considered to be further evidence in support of the contention that no reflected shock wave occurs since the reflected shock temperatures for these runs would be about 4600°K.

In summary, it seems appropriate to review the basic differences in the pyrolysis mechanism for the two simple iodides and to advance suggestions for future work in developing the shock tube techniques for study of more complex, explosive compounds.

In the methyl iodide reaction the route to ethylene appears to be strictly free radical in nature whereas in the ethyl iodide case both molecular and free radical steps are presumably contributors. In both cases, the acetylene formation is assumed to be molecular dehydrogenation of the ethylene.

More precise knowledge of reaction conditions would be obtained if any chance of a reflected shock wave could be eliminated. Expansion of the

shock wave into a much larger volume would cause it to collapse, with no subsequent reflection. By attaching a dump tank to the downstream end of the reaction section, separated by a thin diaphragm which the shock wave would hit and rupture, would permit the shock wave, and the reaction gases, to expand into this previously evacuated volume. Any reflection of a shock wave would be eliminated and the reaction gases could easily be recovered by the method presently used.

The pressure within the shock front exceeds the saturation values of the transducers presently used. Replacement of these transducers with models permitting continuous recording traces of the pressures in the shock tube would provide more accurate information about the shock wave characteristics.

A spectrometer coupled with a streak camera for recording the resolved spectra would obtain data about the reactions within the shock front itself. This would permit examination of reactive intermediates and of reaction products much closer in time to the initial molecular reactions.

It would be desirable to have a chromatograph with variable temperature control to permit faster and more sensitive analysis of the higher molecular weight hydrocarbons. At 105°F the holdup times in the columns of the chromatograph used here are somewhat excessive. This would be very critical in the case of molecules with more than five carbons.

These few improvements would greatly enhance the more precise determination of reaction characteristics and product analysis, permitting better evidence in support of postulated mechanisms. This is of paramount importance in the analysis of the more diverse products obtained from molecules of greater complexity which might be studied in future experimental work.

TABLE 7. DATA ANALYSIS (GAS PHASE PRODUCTS)

METHYL IODIDE RUNS (Average of runs 4, 5, and 6)

<u>MOLE % ETHYLENE-ACETYLENE</u>	<u>MOLES ETHYLENE-ACETYLENE PER MOLE CH_3I REACTED</u>	<u>MOLES ETHYLENE-ACETYLENE EXPECTED ACCORDING TO REACTION (9)</u>
46.6	0.28	0.25

ETHYL IODIDE RUNS (Average of runs 2, 3, and 4)

<u>MOLE % ETHANE REACTED</u>	<u>MOLES ETHANE PER MOLE ETHYL IODIDE</u>	<u>MOLE % ETHYLENE- ACETYLENE</u>	<u>MOLES ETHYLENE-ACETYLENE PER MOLE ETHYL IODIDE REACTED</u>	<u>FROM ETHYLENE- ACETYLENE MEASUREMENT</u>	<u>FROM ETHYLENE- ACETYLENE MEASUREMENT</u>
11.1	0.14	50.6	0.68		
Calculated contribution of reaction (27)			0.72	0.72	
Calculated contribution of reaction (28)			0.28	0.28	

ACKNOWLEDGEMENTS

The authors would like to express their appreciation to:

Dr. Charles F. Rowell for proposing the problem, for his continued interest in the progress of the project and for his assistance in evaluating the data.

Dr. Richard A. Reinhardt for his timely advice and for his critical evaluation of the data.

Mr. Robert Smith for his invaluable assistance in the assembly of the shock tube and associated equipment, especially the electronic timing device.

The Machine Facility under the supervision of Mr. "Scotty" Walker for their most cooperative attitude and their meticulous attention to detail in the fabrication of the shock tube.

